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Title: Catalyst for coal-liquefaction and a manufacturing
method thereof

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Claims

1. A catalyst for coal-liquefaction, made by impregnating porous finely-powdered carbonized-coal obtained by carbonizing (dehydrating) coal, with a water solution containing at least one of iron, nickel and molybdenum.
2. A catalyst for coal-liquefaction, made by impregnating porous finely-powdered carbonized-coal obtained by carbonizing (dehydrating) coal, with a basic water solution of ammonium carbonate, aqueous ammonia, sodium hydroxide, etc. after soaking it into a water solution containing at least one of iron, nickel and molybdenum.

3. A method of manufacturing a catalyst for coal-liquefaction, characterized by

heating coal to higher than 400°C, desirably 600 ~ 800°C at a temperature-raising speed of higher than 10 °C/min, desirably higher than 100 °C/min in an inactive atmosphere,

finely-pulverizing the obtained porous carbonized-coal,

soaking it into a water solution containing at least one of iron, nickel and molybdenum in order to impregnate it with said water solution, and then, dehydrating and drying it.

4. A method of manufacturing a catalyst for coal-liquefaction, characterized by

heating coal to higher than 400°C, desirably 600 ~ 800°C at a temperature-raising speed of higher than 10 °C/min, desirably higher than 100 °C/min in an inactive atmosphere,

finely-pulverizing the obtained porous carbonized-coal,

soaking it into a water solution containing at least one of iron, nickel and molybdenum in order to impregnate it with said water solution,

dripping a basic water solution of ammonium carbonate, aqueous ammonia, sodium hydroxide, etc. onto said carbonized coal, and then, dehydrating and drying it.

Detailed description of the invention

This invention relates to a catalyst used in liquefying coal, and a manufacturing method thereof.

With regard to the coal liquefaction principle, coal which is a high-molecular compound is hydrocracked to be converted into light oil and heavy oil which are low-molecular oils, and ordinarily, the reaction is caused by adding hydrogen to coal at a high temperature and under high pressure. For enhancing the economy of this liquefaction process, the following are important.

(1) The reaction is caused at a low temperature and under low pressure in order to reduce kinetic costs for raising the temperature and pressure, and the costs for facilities should be reduced.

(2) Because hydrogen necessary for liquefaction-reaction is costly, the consumption of hydrogen should be reduced as far as possible. Catalysts for coal liquefaction are used for the effective use of the abovementioned hydrogen and for the alleviation of such conditions as temperature, pressure, etc., and it is desirable to use catalysts which have as high activity as possible.

As catalysts with high activity, such metal oxides as Co, Mo, W, Sn, Fe, etc. and metal-halogenide and so forth are known; and the conditions which should be provided for industrial catalyst(s) are as follows:

(1) The specific gravity thereof should be light so that sedimentation causative of such troubles as clogging may not arise.

(2) To convert asphaltene which is a substance produced by the thermal decomposition of coal, into oil by efficiently

hydrocracking it, the catalyst should be abundant in porosity.

(3) To better the efficiency of contact with coal and hydrogen gas, the particles thereof should be as fine as possible.

(4) The cost should be low.

To meet these conditions, zinc chloride, tin chloride, less-expensive iron-oxide, or iron sulfate, especially disposable red-mud, etc. are ordinarily used industrially. However, in case of inexpensive disposable catalysts such as red mud and so on, the activity is not so high, and hence, it is necessary to add a large amount (about 5 wt% against coal). Thus, there is such a disadvantage as to lead to the high cost of liquefied-oil produced.

As a catalyst which replaces these catalysts, the inventors have developed a recoverable catalyst (Patent Laid-Open No. 1983-1787) for liquefaction. This catalyst is obtained by separating and recovering fine-powder like solid which arises with generated-gas when the residue of liquefied coal is gasified in a steel-bath gasification-furnace, from the gas. This catalyst has the following excellent features:

- * No cost is needed because it can be obtained in a coal-liquefying system.
- * There is no need to pulverize it because it is fine powder.
- * The specific gravity is light because iron-fume has been deposited.
- * It has high activity because it is relatively abundant in porosity.

Moreover, the inventors variously studied (examined) to develop a catalyst for liquefaction which has excellent

properties like the catalyst consisting of fine-dowder like solid produced by the abovementioned steel-bath gasification furnace, and as a result, they found that by using carbonized coal as a carrier (support), a catalyst for liquefaction comparable to the catalyst consisting of the abovementioned fine-powder like solid can be obtained; and this invention has been completed.

The present-invention catalyst for coal liquefaction is characterized in that porous fine-powder like carbonized-coal obtained by carbonizing (dehydrating) coal is impregnated with a water solution containing at least one of iron, nickel and molybdenum, and it is characterized by being impregnated with a basic water-solution of ammonium carbonate, aqueous ammonia, sodium hydroxide, etc., in addition to the abovementioned water solution.

Namely, this invention is characterized by using carbonized coal as a catalyst carrier based on the finding that if coal is carbonized, comparatively porous high-^{specific} ~~ratio~~ surface area carrier is obtained in proportion as the volatile matter is removed. Therefore, as a raw-material coal, coal low in caking(coking)-capacity and high in volatility is desirable. As a raw material for carbonization, timber, plant, etc. are also usable as the case may be. As metal constituents for impregnation for giving catalytic activity to a carbonic carrier (viz. carbonized coal) obtained by carbonizing this coal, iron, nickel and molybdenum which have catalytic activity are selected (enumerated).

As a method for impregnating carbonized coal with these metal constituents, a method of soaking finely-pulverized carbonized-coal into a water solution containing at least one of iron, nickel and molybdenum can be adopted as mentioned later on. If carbonized coal is soaked into the abovementioned water solution, the fine porosities of carbonized coal are impregnated with the solution, and hence, after being soaked, it is dehydrated and dried as it is, so as to be usable as a catalyst for liquefaction.

Furthermore, this invention is characterized by producing (generating) the sediments (hydroxides, etc.) of iron, nickel, etc. in the porosities, by adding a basic water-solution of ammonium carbonate, aqueous ammonia, sodium hydroxide, etc. to the carbonized coal impregnated with the metal constituents of iron, nickel, etc. In this case, after impregnating carbonized coal with the metal constituents of iron, nickel, etc., the abovementioned basic water-solution is dripped for impregnation. The catalytic activity is further enhanced by producing the sediments of the metal constituents impregnated with a basic water-solution like this.

As mentioned above, with regard to the present-invention catalyst for coal liquefaction, porous carbonized-coal has been impregnated with metals having catalytic activity, and further, to enhance the catalytic activity more, the sediments of the metals have been produced in the porosities by dripping a basic constituent. Therefore, it is abundant in the hydrocracking ability, and further, it is not deposited in the reaction tower because its specific gravity is light. Besides, there also exists such an advantage that a catalytic carrier can be manufactured by using the same kind of coal in the

liquefaction-process system.

The method of manufacturing the above catalyst is described below.

The present-invention method of manufacturing a catalyst is characterized by

heating coal to $600 \sim 800^{\circ}\text{C}$ at a temperature-raising speed of higher than $10^{\circ}\text{C}/\text{min}$, desirably higher than $100^{\circ}\text{C}/\text{min}$ in an inactive atmosphere,

finely-pulverizing the obtained porous carbonized-coal,

soaking it into a water solution containing at least one of iron, nickel and molybdenum in order to impregnate it with said water solution, and then, dehydrating and drying it.

As an inactive gas for carbonizing coal, nitrogen, argon, hydrogen, steam and CO_2 are considered, and the exhaust gas evolved by combustion can also be used as the case may be.

The reason for limiting the carbonization-conditions to heating to $400 \sim 800^{\circ}\text{C}$ at a temperature-raising speed of higher than $10^{\circ}\text{C}/\text{min}$ and under an inactive atmosphere is described herein.

To find the conditions for making carbonized coal porous, the inventors variously changed the carbonization-conditions in order to examine (check) the property of carbonized coal corresponding thereto. As a result, they found that there is a mutual relation between the temperature-raising speed, the reached temperature and the property of carbonized coal.

Fig. 1 shows a result gotten by measuring the property of the porosities of carbonized coal obtained by heat-treating

sub-bituminous coal while variously changing the temperature-raising speed. From Fig. 1, it can be seen that in case of the final carbonization-temperature of 600°C , if heated at a temperature-raising speed of higher than $10^{\circ}\text{C}/\text{min}$, the specific surface area of the carbonized coal obtained is $50\text{m}^2/\text{g}$ or more and that it is abundant in micro-porosity-volume. The reason is considered to be that the carbonized coal obtained becomes porous, because the tar produced from coal volatilizes without causing the clogging of the porosities because of the coking of the tar remaining in the porosities in proportion to the increase of the temperature-raising speed.

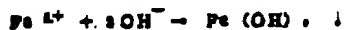
On the other hand, as can be seen from the relation between the final carbonization-temperature and the specific surface area shown in Fig. 2, the final carbonization-temperature is required to be 400°C or more for the specific surface area of $50\text{m}^2/\text{g}$, and even if it is raised to 600°C or more, the effect is not so large. Therefore, the upper limit can be $600 \sim 800^{\circ}\text{C}$.

Based on the above result, in case of the present-invention method, coal is heated to $400^{\circ}\text{C} \sim 800^{\circ}\text{C}$ at a temperature-raising speed of higher than $10^{\circ}\text{C}/\text{min}$ and under an inactive atmosphere in order to obtain carbonized coal abundant in porosity, as coal-carbonization conditions.

Next, in case of the present-invention method, the carbonized coal carbonized in accordance with the abovementioned carbonization conditions is finely pulverized and is soaked into a water-solution containing one of iron, nickel and molybdenum so as to be impregnated with the above metal constituents having catalytic activity. In this case, boiling, stirring, etc. are done for impregnation. Therefore, the carbonized coal is dehydrated. As a method thereof, for example, the

reduced-pressure filtration method can be used. After being dehydrated, the carbonized coal impregnated with a water solution is dried as it is, and it is used as a catalyst for liquefaction.

Moreover, in case of the present-invention method, ion-exchanged water is added to carbonized coal impregnated with the above metal constituents, and while measuring pH, a basic water-solution of ammonium carbonate, aqueous ammonia, sodium hydroxide, etc. is dripped, to make the sediment of the above metal constituents in porosities. In case of iron, the reaction formula at this time is as follows:



Then, this carbonized coal is dried under reduced pressure and is used as a catalyst for liquefaction.

As for the use of the abovementioned catalyst for liquefaction, it can also be pre-sulfurated by a compound containing sulfur in advance, or it can also be added to a raw-material slurry together with single sulfur. In this case, iron, molybdenum, etc. exhibit hydrogenation activity in a form of sulfide.

According to the present-invention method, a catalytic carrier abundant in porosity can be obtained by simply controlling the temperature-raising speed and the heating temperature at a heating furnace. In addition, because the carrier itself is carbonized coal, the production can be done using the same kind of coal in a liquefaction-process system. The product catalyst is manufactured through a process of carbonization--soaking--dehydration--drying, but in case of these respective processes, existing facilities and apparatuses can be used, and hence, the catalyst-production cost does not

become large. Therefore, a highly-active catalyst for liquefaction can be produced at a comparatively-lower cost.

With reference to the amount-to-be-added of the present-invention catalyst for liquefaction, the larger the better. However, if a too large amount is added, minerals in the liquefaction residue are increased although the liquefaction rate (ratio) under the same reaction-conditions increases; and this matter threatens to cause troubles in such processes as the separation of solid from the liquid, and reduced-pressure distillation, etc. Therefore, the amount of the catalyst to be added is 0.1 ~ 10 wt%, desirably 1 ~ 5 wt%, against the carbonized coal to be liquefied.

The examples of the experiments for coal liquefaction carried out by using the present-invention catalyst are described below.

Example 1

The sub-bituminous coal with the property shown in Table 1 was carbonized using an infrared-ray type rapid-heating apparatus under the following conditions:

- * Temperature-raising speed: 60°C/min
- * Time: 1 minute
- * Final carbonization temperature: 600 °C

Regarding the examined structure of the porosities of the carbonized coal, the specific surface area was 113 m²/g, and the volume of the porosities was 0.28 cc/g. Next, 8 g of this porous carbonized-coal was finely-pulverized by a pulverizing machine so as to be 400 mesh or less, and then, 20 g of ion-exchanged water and 200 g of ferric nitrate [iron (III) nitrate] ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were added and mixed. This mixture was soaked into an iron nitrate water-solution adjusted by being

heated, and boiling and stirring were done for 30 minutes. Thus, the carbonized coal was impregnated with the iron nitrate water-solution. After that, by the filtration under reduced pressure, the carbonized coal alone impregnated with the iron nitrate water-solution was taken out. Furthermore, ion-exchanged water was added to 6.3 g of the catalyst A obtained by being dried in vacuo for 1 hour at 110°C, and the carbonized coal impregnated with the iron nitrate water-solution, and while measuring pH, an ammonia carbonate water-solution was dripped, and when pH became 8, the dripping was stopped. Then, after separating the carbonized coal by performing the filtration under reduced pressure again, 300 g of the coal with the property shown in Table 1 was liquefied separately under the conditions shown in Table 2, using 6.3 g of the catalyst B obtained by being dried in vacuo for 1 hour at 110 °C. As a catalyst for liquefaction, 3.6 g each of single sulfur was used in addition to the above A and B.

Moreover, for comparison, coal with the property shown in Table 1 was liquefied under the same conditions shown in Table 2, using 12.6 g of red mud (iron content: 35 wt%) C and 3.6 g of single sulfur as catalysts.

As for the respective liquefied-products, the total amount of the mixture consisting of solid and liquid was subjected to single distillation after performing gas-analysis, to find the yield of liquefaction. The result is shown in Table 3. The definition of the liquid yield is in accordance with the following formula:

Liquid yield = (C, ~ fraction with a boiling point of 538 °C

100

- amount of raw-material solvent) x $\frac{\text{Amount of moisture-free coal used}}{\text{Amount of moisture-free coal used}}$

From Table 3, it can be seen that although each used amount of the catalysts A and B for liquefaction manufactured in accordance with the method of this invention is smaller than the used amount of red mud, the high yield of liquid can be obtained.

Table 1 Property of coal

Industrial analysis 工業分析 元素分析 石炭の性質

工業分析			元素分析		
灰分	VM	FSI	Ro	Tr	
8.0wt%	48.7wt%	0	0.43	56.3	

Ash content

Element analysis 元素分析 (wt% dry)

C	H	N	S	O
76.18	5.74	0.99	0.21	16.88

Table 2 Conditions for liquefaction-reaction

Liquefaction-

reaction

Electromagnetic induction stirring-type

apparatus

autoclave

Coal

300 g of coal with the property shown in
Table 1

Solvent

600 g of a fraction with a boiling point of
180 ~ 450°C out of the products obtained by
hydrogenating a mixture of naphthalene :
absorbable oil *¹ : anthracene oil *² = 10 :
45 : 45 by using a Mo-Ni-Al₂O₃ catalyst under
the reaction conditions of 350 °C and 1 hour

Reaction temp.

450°C

Reaction time

1 hour

Reaction

Initial hydrogen-pressure 70 kg/cm²G

pressure

(Reaction pressure corresponding to 170 kg/
cm²G)*¹ Tar fraction with a boiling point of 250 ~ 300°C*² Tar fraction with a boiling point of 300 ~ 400°C

Table 3 Result

Constituents
Catalysts

第3表

Liquid yield

触媒	成分	液収率 (wt%)
A	Fe 30% C 45%	50
B	Fe 25% C 40%	52
C	Fe 30% Al ₂ O ₃ 55%	48

Example 2

Eight grams of carbonized coal by quite the same method as that in Example 1 using coal with the property shown in Table 1 was soaked into a water solution consisting of 20 g of ion-exchanged water, 20 g of nickel nitrate and 200 g of ferric nitrate [iron (III) nitrate], and boiling and stirring were done for 30 minutes, and the carbonized coal was impregnated with said water solution. Thereafter, using 1.2 wt% of single sulfur and 2.1 wt% of the catalyst D obtained by drying in vacuo the carbonized coal separated by reduced-pressure filtration, the coal shown in Table 1 was liquefied under the conditions shown in Table 2 like Example 1.

From Table 4, it can be seen that by adopting such 2 elements as Fe-Ni, catalytic activity is further enhanced, to raise the yield of liquid.

Table 4 Result

Constituents
Catalysts

第4表

Liquid yield

触媒	成分	液収率 (wt%)
D	Fe 25% Ni 9% C 61%	54

Example 3

Ten grams of the carbonized coal obtained by carbonizing the coal shown in Table 1 by an electric furnace for 1 hour at a temperature-raising speed of 50 °C/min and at the final carbonization temperature of 600°C was soaked into a water solution prepared by dissolving 53 g of ammonium molybdate in 150 cc of aqueous ammonia and by adding 30 g of nickel nitrate. Thereafter, using 1.2 wt% of simple sulfur and 2.1 wt% of the catalyst E obtained by the same method as that in Example 2, the coal shown in Table 1 was liquefied under the conditions shown in Table 2.

From Table 5, it can be seen that the high yield of liquefaction is exhibited also in case of this example.

Table 5 Result

Catalysts	第 5 表 結 果			Constituents
	種 類	成 分	濃 度 率 (wt%)	Liquid yield
E		Mo 10%	88	
		Ni 2%		
		C 88%		

Simple description of the drawing

Fig. 1 is a graph showing the relation between the temperature-raising speed and the property of the porosities of carbonized coal in this invention, and Fig. 2 is a graph showing the relation between the final carbonization temperature and the specific surface area.

